Electron Beam-Generated Plasmas for Polymer Surface Modification

S.G. Walton, Plasma Physics Division, U.S. Naval Research Laboratory, Washington, DC; E.H. Lock, NRL/NRC Postdoctoral Research Associate, Washington, DC; D. Leonhardt, Fusion UV Systems, Inc., Washington, DC; and R.F. Fernsler, Plasma Physics Division, US Naval Research Laboratory, Washington, DC

ABSTRACT

The Naval Research Laboratory has developed a plasma processing system for use in a variety of materials processing applications ranging from etching to deposition. The plasma in this system is produced by high-energy (≈ 2 keV) electron beams. These plasmas have properties that separate them from conventional discharges, making them well-suited for a number of applications, including the processing of delicate materials. In this paper, we discuss the use of these plasmas for polymer modification.

INTRODUCTION

The Naval Research Laboratory has developed a materials processing system based on electron beam-generated plasmas for use in a range of applications [1,2]. When high-energy (≈ 2 keV) electron beams are used as the primary ionization source, the resultant plasmas have several unique characteristics when compared to conventional low-pressure plasma sources:

Localized plasma source. The geometry of the plasma source is related to the electron beam dimensions, and beam thicknesses of 1 cm are typical. The plasma production region is limited to the beam volume, which is well defined and uniform when the beam is magnetically collimated. (Fields of approximately 150 gauss are sufficient to minimize beam spreading systems up to 1 m long.) Outside the beam channel, the plasma density and ion composition are altered by ion-electron and ion-neutral reactions, so electrodes (or substrates) can be independently positioned to take advantage of the changes in the outwardly diffusing flux of ions and radicals. This is in contrast to conventional discharges, where the boundaries of the ionization region are not well defined and increasing the dimensions in a uniform manner can be problematic. Thus, it is possible to carefully control the ion flux by moving the substrate position [3].

Controllable species production. Conventional plasma discharges rely on externally applied electric fields to raise the plasma electron temperature enough to ionize the gas and sustain the plasma. In such discharges, inelastic collisions (excitation and dissociation) consume most of the delivered energy, and species production favors the species with the lowest creation thresholds. For multi-kilovolt electrons passing through a gas, ionization is always the dominant interaction (followed by excitation or dissociation) and the cross-sections are similar for all processing gases. Thus, species generation can be directly regulated by adjusting the background gas concentrations [3].

Low electron temperature. In discharges, the electron temperature is typically above 2 eV and since the electron temperature determines the plasma potential, ions incident to adjacent surfaces will have energies that are usually a factor of about 5 times the electron temperature. Because the high-energy electron beam ionizes the gas and there is no heating applied to the plasma electrons, plasma electrons are rapidly cooled by inelastic collisions. (Electrostatic cooling also reduces the electron temperature, which is particularly important in noble gases.) The resulting plasma electron temperature varies with the working gas, but is ≤ 1 eV in all gases [3,4]. The temperature in molecular gas backgrounds tends to be lower than in noble gases due to the availability of low-energy excitation states. In the case of nitrogen, the lowest excitation levels are a few tenths of an electron volt. Thus, in molecular gases, ions incident to grounded surfaces will exhibit energies below 2 eV [3].

All of these attributes can be advantageous in the processing of polymers, but the most important is the control over the intensity of the ion flux and the low incident ion energies. In conventional discharges, ion energies typically exceed 10 eV, which is above the sputtering threshold for many materials. In electron beam produced plasmas, the incident ion energies are approximately the surface binding energies of common species. The result is a process that has the benefits of both plasma processing and very high temperature wet processes, without the drawbacks of either approach. In beam-produced plasmas, we expect to find chemical changes similar to those observed using discharges but without the surface or subsurface damage. In this respect, modification may be viewed as a process involving only a monolayer or two.

EXPERIMENTAL

The experimental apparatus has been discussed previously [5] and is shown in the schematic of Figure 1. The system vacuum was maintained by a 250 l/s turbo pump, with a base pressure on the order of 10^{-7} Torr. The operating pressure was achieved by introducing high-purity gases through

© **2007 Society of Vacuum Coaters** 505/856-7188

50th Annual Technical Conference Proceedings (2007) ISSN 0737-5921

mass flow controllers and throttling the turbo pump using a manual gate valve.

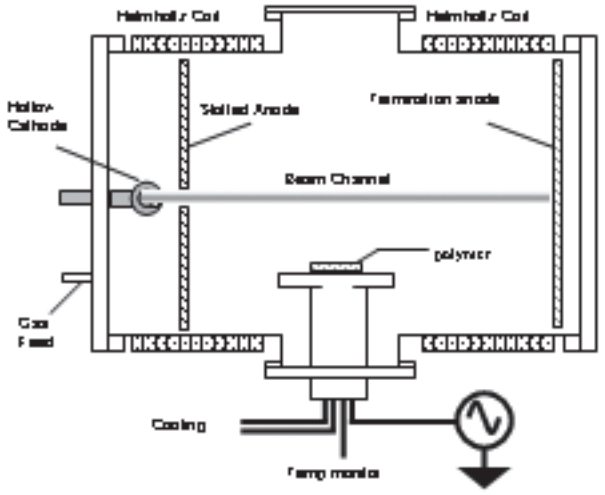

Figure 1: A schematic diagram of the processing system.

The electron beam was produced by applying a 2 kV pulse to a linear hollow cathode for a selected pulse duration and duty. The emergent beam passed through a slot in a grounded anode and was then terminated at a second grounded anode located further downstream. The electron beam volume between the two anodes defines the ionization source volume, with the dimensions set by the slot size (1 cm x 25 cm) and the anode-to-anode length (40 cm). Beam spreading from collisions with the neutral background was largely eliminated by a co-axial magnetic field that was produced by a set of external magnetic field coils.

For the plasma diagnostics, the magnetic field was turned off in an effort to improve the instrument detection of neutrals. The ion flux and neutral density were measured at the center of a grounded 5.7 cm diameter stainless steel electrode using a Hiden EQP 300 Plasma Probe, positioned at the same location as the substrates during processing. Species enter the EQP through a 50 μm diameter aperture located in the center of the electrode and are first energy selected by an electrostatic energy analyzer (EA) and then mass filtered by a quadrupole mass spectrometer (QMS). The energy analyzer has a fixed resolution ($\Delta E/E_t$) that provides an uncertainty in energy of approximately ± 0.15 eV. For the ion flux measurements, data acquisition is time-resolved and the gating techniques have been described elsewhere [6]. The EQP has not been calibrated to determine the absolute flux of each species, so the intensity of the measured signal is reported in arbitrary units.

For the processing experiments, thin Kapton tape (Saint-Gobain) and 1.6 mm thick high density Polyethylene (Mc-Master-Carr) was used. Prior to treatment, all samples were cleaned in methanol. The samples were then placed on a stage, which was inserted so that the substrate surfaces were parallel to the electron beam at a distane of 1.5 cm from the beam axis. Prior to each exposure, the chamber was evacuated to a base pressure less than 10^{-6} Torr. The total processing time, operating pressure and magnetic field were held constant at 10 minutes, 60 mTorr and 210 Gauss, respectively. Several processing conditions were employed by varying the plasma duty (20-40%) and gas flow rates (Ar: 60, 25 sccm; SF_6: 16, 10 sccm). After treatment, the chamber was evacuated to a pressure less than 10^{-5} Torr. The samples were then removed from vacuum to perform *ex-situ* surface diagnostics.

In order to determine changes in the surface properties of the polymers, the Zisman method [7] was used to estimate the critical surface tension (or surface energy) of both untreated and plasma treated samples. For this method, the contact angle of various liquids are measured, and the cosine of those angles are plotted as a function of the liquid surface tension. The sample critical surface tension can be estimated by extrapolating the data to $\cos\theta = 1$. The contact angle of various liquids was determined using a goniometer and the drop volume was approximately 2 microliters. Table 1 gives the liquids used and their critical surface tensions. For liquids from the same homologous series (octane, dodecane, and hexadecane), the data was fitted with a straight line. For combinations of liquids, the data was fitted using the approach of Fowkes ($x^{-1/2}$) [7] to determine the polymer critical surface tension.

Table 1

Liquid	Surface tension (dynes/cm)
Octane	22
Methanol	23
Dodecane	25
Hexadecane	28
1,4-Dioxane	33
Benzylalchohol	39
Ethylene Glycol	48
Ammonium Hydroxide	63
Water	73

RESULTS AND DISCUSSION

Plasmas Diagnostics

Shown in Figures 2 and 3 are the ion spectrum and ion energy distribution measured at a floating electrode located 1.5 cm from the beam axis. For these measurements, the operating pressure was 60 mTorr and the argon and SF_6 flows were 25 and 10 sccm respectively. Shown in Figure 4 is a relative difference spectrum determined by subtracting the neutral density spectrum while the plasma is on, from the spectrum while the plasma is off (and then normalizing by the off spectrum).

Since these measurements are time-averaged, the plasma-on and plasma-off measurements were taken over comparable amounts of time.

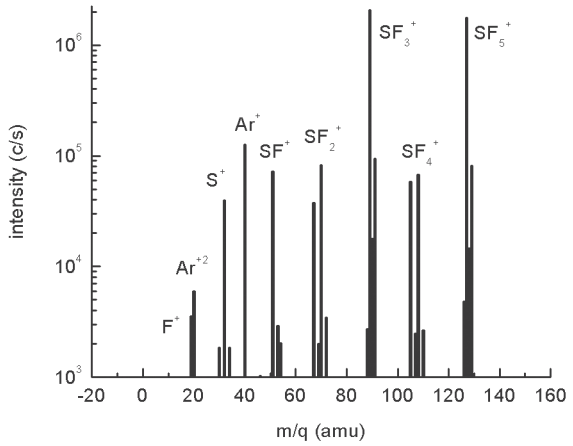

Figure 2: Ion mass spectrum measure at electrodes located adjacent to plasmas produced in Ar/SF_6 mixtures.

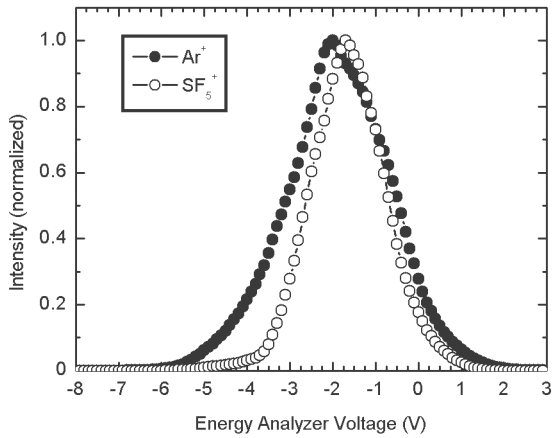

Figure 3: Ion energy distribution at surfaces located adjacent to plasmas produced in Ar/SF_6 mixtures.

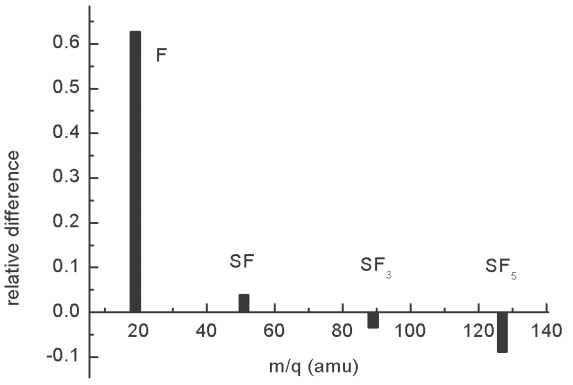

Figure 4: A relative difference spectrum comparing the neutral density spectrum while the plasma is running with the neutral density spectrum in the absence of plasma.

Compared to measurements in discharges containing mixtures of SF_6, the ion mass spectrum tends to have a larger fraction of lower mass SF_6 species since the cross sections for dissociative ionization are larger at higher electron energies. The large loss of Ar^+ is a result of charge exchange reactions with SF_6. The ion energies shown in Figure 3 are plotted as a function of energy analyzer voltage rather than energy. In electronegative gases (SF_6 or O_2), it is not uncommon to have surface charging, and so the distribution appears at negative voltage values since the energy analyzer is referenced to ground. This of course makes it difficult to determine the true energy, although it is clearly low since the distribution extends only to about 1 Volt.

The neutral spectrum is indicative of the dissociation of the background gas. The daughter species (SF_5, SF_4, and SF_3) decrease when the plasma is on, while the amount of fluorine increases. Meaning there is less SF_6 present and more F while the plasma is on. In separate work, where the gas flow was reduced to near zero, we have estimated the dissociation fraction to be between 5 and 10%. For the operating conditions in this work, it is assumed to be less than 5%.

Polymer Processing

The estimated critical surface tension of untreated samples and those exposed to plasmas produced in pure argon and Ar/SF_6 mixtures are shown in Figures 5-7.

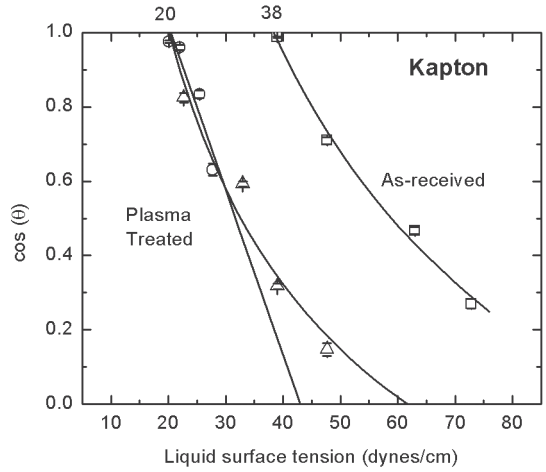

Figure 5: Zisman plot for untreated and plasma-treated kapton. The straight line fits the polar liquids.

Treating the samples in plasmas produced in Ar/SF_6 mixtures decreased the critical surface tension, which results in a more hydrophobic surface. For Kapton, the critical surface tension was reduced by nearly 50%. For polyethylene, the critical surface tension was reduced by about 36%. Treating the polyethylene with a plasma produced in pure argon increased the critical surface tension by approximately 36%, resulting in a more hydrophilic surface. Since argon is inert, this increase in critical surface tension is thought to be caused by oxygen

adsorption when the sample was exposed to the atmosphere after treatment. The bombardment of the surface with argon ions is assumed to create active bonding sites that, when exposed to air, readily react with oxygen.

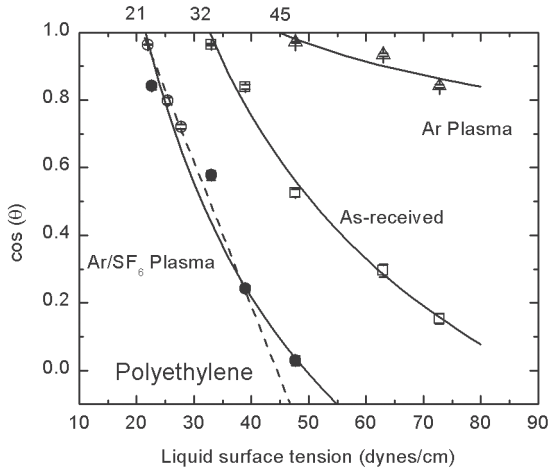

Figure 6: Zisman plot for untreated polyethylene and polyethylene treated in plasmas produced in argon and argon/SF_6 mixtures. The straight line fits the polar liquids.

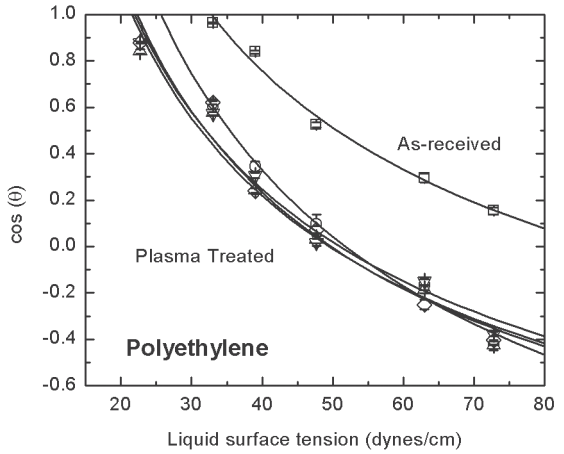

Figure 7: Zisman plot for untreated polyethylene and polyethylene treated in plasmas produced argon/SF6 mixtures operating at various duty factors and gas flows.

The critical surface tension shows no strong dependence on either the plasma duty or operating gas flow for polyethylene samples (Figure 7). The results are found to be similar for Kapton. For a constant treatment time, changing the plasma duty factor would vary the time for which the ions are incident at the surface. If the changes in the surface were the result of ion bombardment (e.g. a sputter-induced change in morphology), there should be a correlation to the duty factor. Changing the gas flow rate on the other hand, should only alter reactive neutral species flux. Thus, it would seem that the surface modification is largely a chemical one.

SUMMARY

Experiments designed to investigate the treatment of polymers with electron beam-generated plasmas produced in argon and mixtures of argon and SF_6 were performed. Plasma diagnostics showed that the incident ions have low energies and the background gas is weakly dissociated. The critical surface tension of both kapton and polyethylene was lowered when exposed to plasma produced in SF_6 mixtures. When pure argon was used the critical surface tension of polyethylene was found to increase. These changes were correlated to a change in surface chemistry. Studies are underway to better understand the role of low-energy ions in the modification of polymers.

ACKNOWLEDGEMENTS

This work is supported by the Office of Naval Research. EHL appreciates the support of the National Research Council.

REFERENCES

1. D. Leonhardt, C. Muratore, S.G. Walton, and R.A. Meger, "Plasma Enhanced Surface Treatments Using Electron Beam-generated Plasmas," *Surf. Coat. Technol.* **188-189**, 299 (2004).

2. D. Leonhardt, S. G. Walton, and R. F. Fernsler, "Fundamentals and applications of a plasma-processing system based on electron-beam ionization," *Phys. Plasmas* **14**, 057103 (2007).

3. S.G. Walton, C. Muratore, D. Leonhardt, R.F. Fernsler, D.D. Blackwell, and R.A. Meger, "Electron beam-generated plasmas for materials processing," *Surf. Coat. Technol.*, **186 (1-2)**, 40 (2004).

4. D. Leonhardt, S.G. Walton, D.D. Blackwell, W.E. Amatucci, D.P. Murphy, R.F. Fernsler, and R.A. Meger, "Plasma diagnostics in LAPPS," *J. Vac. Sci. Technol.* A, **19 (4)**, 1367 (2001).

5. D. Leonhardt, S.G. Walton, C. Muratore, F. Fernsler, R.A. Meger, "Etching with Electron Beam Generated Plasmas," *J. Vac. Sci. Technol.* A **22 (6)**, 2276 (2004).

6. S.G. Walton, D. Leonhardt, and R.F. Fernsler, "Time-resolved Diagnostics in a Pulsed, Electron Beam-Generated Plasma," *IEEE Trans. Plas. Sci.* **33,** 838 (2005).

7. H.W. Fox and W.A. Zisman, *J. Coll. Sci.* **5**, 514 (1950).

8. F.M. Fowkes, *Ind. Eng. Chem.* **56**, 40 (1964).